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Erna Gevondyan
College of DuPage

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Nuclear Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

by Erna Gevondyan

(Physics)

Abstract

Thermophysical properties such as thermal expansion, heat capacity, oxygen diffusion, and thermal conductivity of uranium dioxide at different stoichiometry compositions were evaluated in the temperature range of 300 – 3000 K by molecular dynamics simulation, using Arima's potential. The negative effect of oxygen non-stoichiometry in uranium dioxide $UO_{2\pm x}$ on the thermal expansion and the heat capacity has been discussed. The calculated oxygen diffusion coefficient demonstrates more favorable results in terms of defective structures when compared to perfect lattice structures. The negative effect of the increase in temperature and the change in composition on thermal conductivity of uranium dioxide agrees with the previous observations.

1. Introduction

The study of nuclear fuels has played an important role in the energy resources research. In particular, a lot of research has been conducted on the thermophysical properties of uranium dioxide (UO_2) in the past. [1] [2] A profound understanding of these properties is needed in order to correctly assess certain aspects in the development and maintenance of nuclear reactor systems, as well as the effective utilization of the material. Many properties of nuclear materials have been evaluated through experimental studies, however there are often limitations associated with effective conduction of these experiments. Such limitations may include rules and regulations, equipment limitation, overall safety in terms of radiation, and so on. Therefore, computational techniques have proven to be an effective tool in the prediction and evaluation of certain properties of nuclear materials at extreme conditions. [1] [2] The objective of this study is to assess the effects of non-stoichiometry and temperature on the thermophysical properties of uranium dioxide by performing equilibrium molecular dynamics simulations (EMD).

2. Computational setup

2.1. Molecular dynamics simulation

The thermophysical properties studied in this paper were calculated and evaluated using the LAMMPS Molecular Dynamics Simulator software. [3] The fluorite structured cells of uranium dioxide (face centered cubic (FCC) lattice of uranium, and simple cubic lattice of oxygen) were constructed using a Python™ script. Each stoichiometric conventional unit cell contains four U^{4+} and eight O^{2-} lattice ions. The construction consists of creating uranium and oxygen ions, and placing them into their lattice and interstitial sites. The atomic positions establish the initial condition of the simulation cell. The assembly created for the calculation of thermophysical properties consisted of a 6×6×6 construction of fluorite unit cells (864 cations and 1728 anions), and a 5×5×5 assembly for the calculation of thermal conductivity (500 cations and 1000 anions). The data was then extracted and implemented into a LAMMPS input file. The input file accepts potential parameter values into a preset function ("born-coul-long", in this case), and uses them along with the implemented data of

the created block of unit cells, in order to run the simulation. The MD simulations results were evaluated based on a 100 ps. evaluation, and a 50 ps. equilibration time. The temperature range for the thermophysical properties was 300K to 3000K, using an NPT ensemble, and 300K to 2000K for thermal conductivity, using the NVE ensemble.

2.2. Non-stoichiometry

The defect structure of hyper-stoichiometric uranium dioxide has been studied in detail by Willis. [4] In the present study, different compositions of $UO_{2\pm x}$ were analyzed, where the values of x ranged from -0.04 to 0.10, which meant extraction of oxygen ions from their lattice sites (hypo-stoichiometry), or addition of oxygen ions into interstitial sites (hyper-stoichiometry). The interstitial sites for additional oxygen ions follow octahedral symmetry. The chosen algorithm for the arrangement of ions in the defective cells involved a random sampling module in Python. Since the extraction or the addition of the oxygen ions, causes a misbalance of charge in the simulation cell, the charge of some uranium atoms was changed to ensure neutrality. In the case of hypo-stoichiometry, where the extraction of oxygen ions created excess positive charge, some of the U^{4+} ions were randomly replaced with U^{3+} ions. On the other hand, in the case of hyper-stoichiometry, excess negative charge created by the added interstitial oxygen ions was compensated by a random replacement of U^{4+} ions with U^{5+} ions. In both cases, the ratio of replaced uranium to added/extracted oxygen is 2:1.

2.3. Potential parameters

The interatomic potential parameters for U^{4+}, U^{5+}, and O^{2-} atoms used for this simulation were extracted from the literature by Arima et al. [1] The parameters used for the U^{3+} ion were obtained from the literature by Nichenko et al. [2] These parameters were then utilized by the simulation software in the order of the following equation:

$$U(r) = \frac{z_i z_j e^2}{r} + f_0\left(b_i + b_j\right)\exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) - \frac{c_i c_j}{r^6} \qquad (1)$$

Equation (1) portrays a classical BMH type potential with a partially ionic model of 67.5% iconicity. [1] Therefore, z_i and z_j are the effective ionic charges of ions *i* and *j* respectively (e.g. the effective charge of U^{4+} becomes $+4 \times .675 = +2.7$); *r* is the distance between the ions *i* and *j*; f_0 is the adjustable force parameter; *a*, *b*, and *c* are potential parameters given to ions *i* and *j*. The author's choice to use 67.5% ionicity was influenced by a study done by Inaba et al. [5]

3. Results and discussion

3.1. Lattice parameters and linear thermal expansion of uranium dioxide

The lattice constant of stoichiometric uranium dioxide was calculated and evaluated as a function of temperature. Considering the geometry of the fluorite structure, the easiest way to compute the lattice constant at each temperature was to take the cube root of the average volume of the entire simulation cell at a certain temperature, and divide it by 6 (i.e. 6×6×6 cell). The results obtained by calculating the stoichiometric composition of UO_2 closely matched the experimental data, [6] and are depicted in Fig.1 (a). A similar method was then used in order to calculate the lattice constants of non-stoichiometric compositions of uranium dioxide. When the results were compared to each other, a general pattern of similarity in the growth of the lattice constant was observed in each composition. These results also confirmed a previously made observation by Yakub et al., [7] which stated that the lattice parameter of hyper-stoichiometric UO_{2+x} generally decreases with the addition of interstitial oxygen ions (increase the value of *x*) at a given temperature. This observation held

consistent with the one made in this work for the temperature range of 300K < *T* < 1600K. However, at *T* > 1600K, a slight increase in the lattice parameter is observed (Fig.1 (b)).

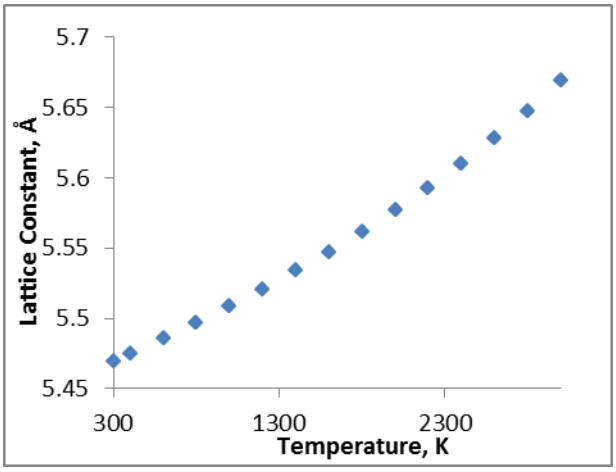

Fig. 1 (a). Lattice constant of stoichiometric UO2 as a function of temperature

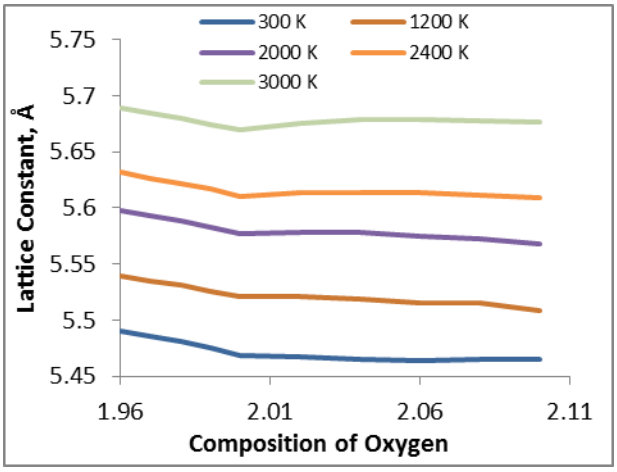

Fig. 1 (b). Lattice constant at several different temperatures as a function of composition

Once all of the lattice parameter data was retrieved and plotted against temperature, a third-order polynomial was then fitted to each curve. The choice of the order of the polynomials was influenced by the work of Martin et al. [8] The interpolation function used to represent the lattice constant change with respect to temperature had the general form of:

$$L(T) = a + bT + cT^2 + dT^3, \qquad (2)$$

where *L* is the lattice constant at *T*, and *a*, *b*, c, and *d* are the coefficients of *T* at each non-

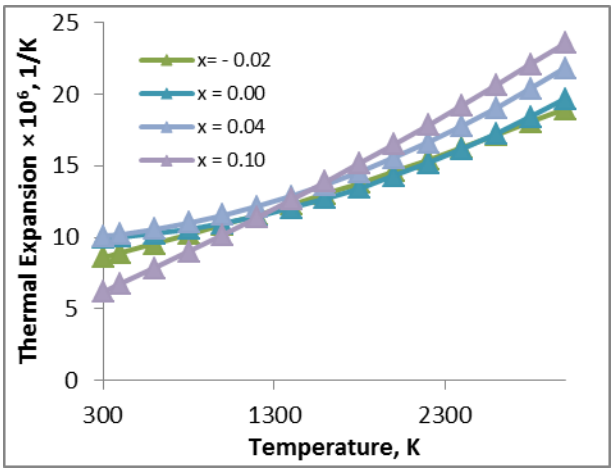

Fig. 2 (a). Linear thermal expansion of different compositions of non-stoichiometric UO2±x as a function of temperature

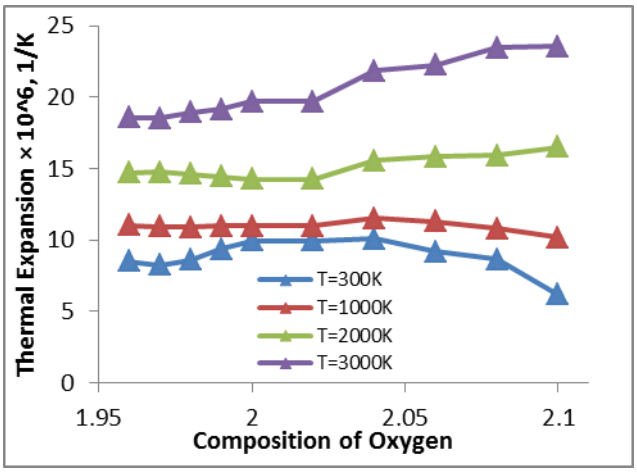

Fig. 2 (b). Linear thermal expansion at different temperatures of UO2±x as a function of composition

stoichiometric composition. The corresponding instantaneous linear thermal expansion, defined as $(1/L_{300})(\partial L/\partial T)$ can then be readily evaluated from eq. (2) for each composition of $UO_{2\pm x}$. Figures 2 (a) and (b) depict the values of thermal expansion obtained from these calculations as functions of temperature and composition respectively. The results demonstrate a pattern of increase of the lattice

parameters with the increase of temperature, and their decrease with the increase in composition of oxygen, which agrees with Yakub's observation.

3.2. Enthalpy and heat capacity of uranium dioxide

As mentioned in the introduction, the enthalpy of the system in this MD simulation was calculated using the NPT ensemble, which means that the pressure was kept constant. Average enthalpy values for each temperature run of the stoichiometric uranium dioxide were extracted and plotted against temperature. The data values in this plot closely matched those described by Fink et al., [9] which is considered a good synthesis of data from literature. A similar method was then used in order to calculate the average enthalpy.

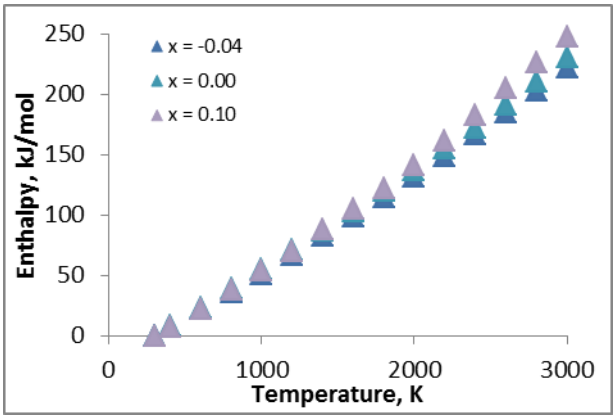

Fig. 3. Enthalpy of the simulated system of different compositions of UO2±x as a function of temperature of the non-stoichiometric compositions, although the enthalpy had to be normalized by multiples of $(3 + x)/3$ and $(3 - x)/3$ for hyper- and hypo-stoichiometric compositions respectively.

Fig. 3 depicts the enthalpy of several compositions of $UO_{2\pm x}$ as a function of temperature. Similarly to the results for the lattice constant calculation, the enthalpy values for each composition have a common general trend of growth with the increase of temperature. In the temperature range of $300 < T < 1000$ the enthalpy function for each composition represents rather a linear function, however at $T > 1000$, it acquires a more exponential behavior.

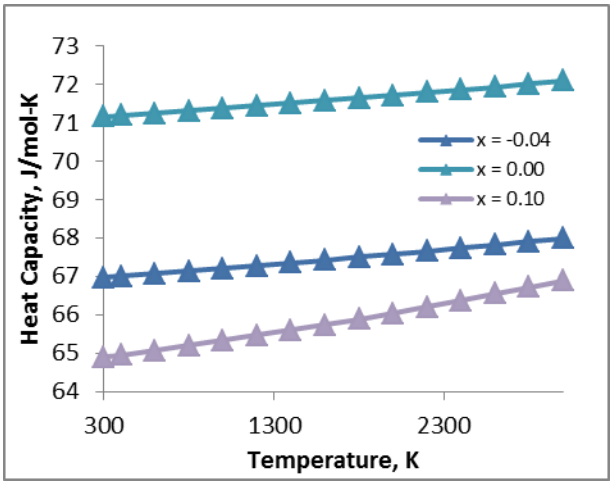

Fig. 4 (a). Heat capacity of different non-stoichiometric compositions of UO2±x as a function of temperature

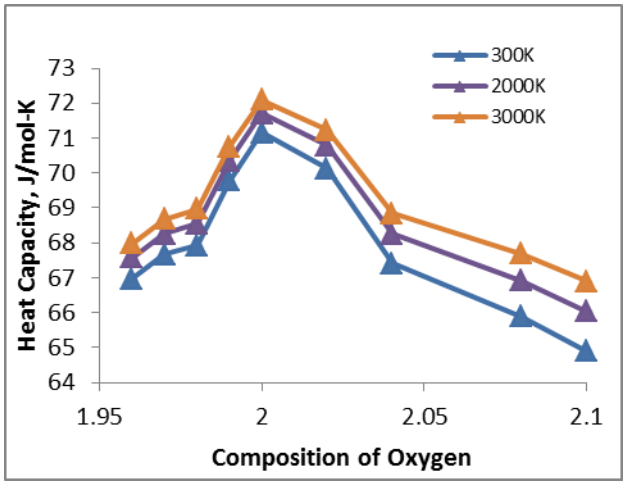

Fig. 4 (b). Heat capacity at different temperatures of UO2±x as a function of composition

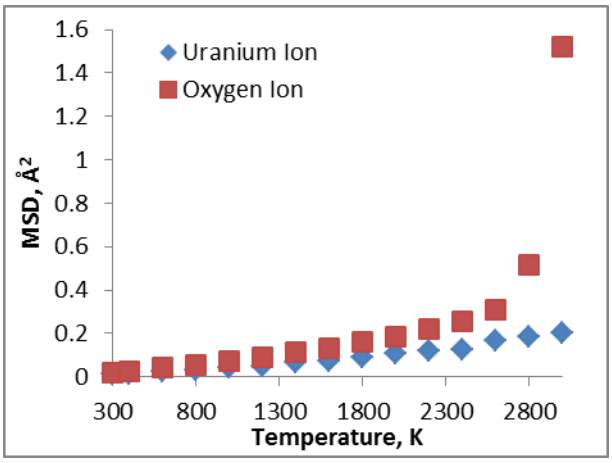

Fig. 5. Mean square displacement of the oxygen and uranium ions in the stoichiometric UO2 structurein agreement with Fink's.

The choice of the NPT ensemble was partially influenced by the simplicity of the calculation of the instantaneous heat capacity with the change of temperature of every composition of $UO_{2\pm x}$. In order to do this, a second order polynomial was fitted to each enthalpy function curve for every composition. The polynomials had a general form of:

$$H(T) = a + bT + cT^2, \quad (3)$$

where $H(T)$ is the average enthalpy value at a given temperature, and a, b, and c are the coefficients of T at each non-stoichiometric composition. The heat capacity at constant pressure, C_p, as a temperature derivative of enthalpy ($\partial H(T)/\partial T$) can be readily calculated using eq. (3). The values of C_p were then plotted against temperature. Fig. 4(a) demonstrates a general increasing pattern of the heat capacity with the increase in temperature. However, it is also obvious that the stoichiometric structure holds the highest heat capacity at any temperature, in comparison with both hypo- and hyper-stoichiometric structures. In order to better illustrate this behavior, the values of heat capacity at several different temperatures were plotted against composition. Fig. 4 (b) clearly illustrates the predominance of the perfect composition at any temperature in terms of heat capacity.

3.3. Oxygen Diffusion in uranium dioxide

The method for calculation of diffusion of oxygen was adopted from the work of Basak et al., [10] who began by calculating the mean square displacement (MSD) of oxygen and uranium ions. Following Basak's method, the calculations were first performed for the stoichiometric composition of uranium dioxide.

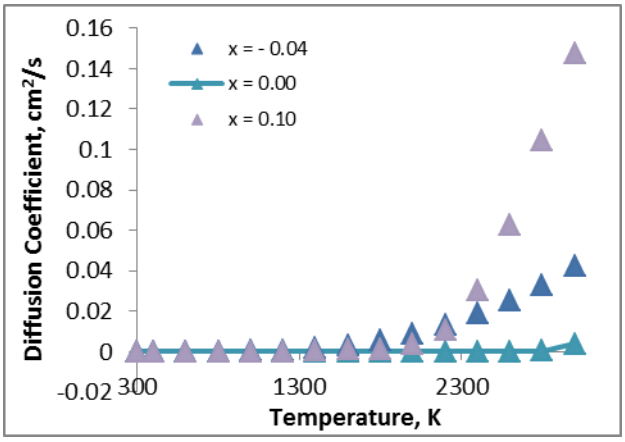

Fig. 6 (a). Diffusion coefficient of oxygen of different non-stoichiometric compositions of UO2±x as a function of temperature

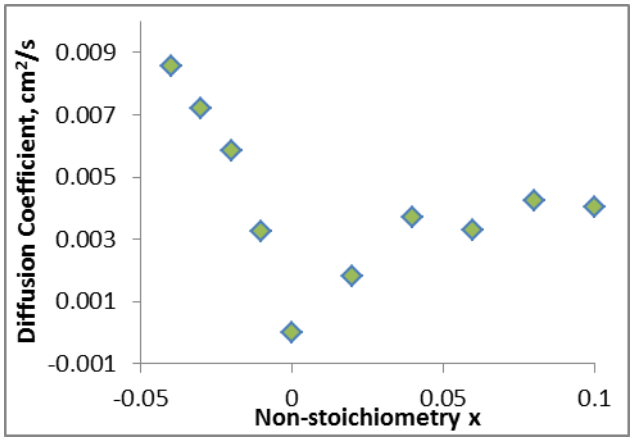

Fig. 6 (b). Diffusion coefficient of oxygen at 2000K as a function of composition

In this simulation, MSD values at each time step were extracted directly from the calculation performed by LAMMPS. MSD was plotted against time for each temperature run. These plots showed that the Bredig [11] transition began in the range of 2500 – 2800K. Our results slightly disagree with Basak's, who reported a 2300 – 2700K range. This can be explained by the fact that, unlike this work, Basak used a 3×3×3 simulation cell, which means a larger surface/core ion ratio than that of this work. However, the general trends in the behavior agreed otherwise, as demonstrated in Fig. 5. The diffusion coefficients were then calculated by using the Einstein relation:

$$D_i = Lt_{t\to\infty} \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle, \quad (4)$$

where D_i is the diffusivity of the ion *i*, and *r* is the location of *i* at the time *t*.

Subsequently, the calculation of oxygen diffusivity of the different non-stoichiometric uranium dioxide compositions was performed following the same principle. The calculated values were once again extracted from the software and evaluated using the Einstein relation to determine the diffusion coefficients of each composition at different temperatures.

Fig. 6 (a) shows a plot of the diffusion coefficient of oxygen ions at different compositions as a function of temperature. The diagram clearly demonstrates that the defect compositions of uranium dioxide have a higher rate of oxygen diffusion within a significantly lower temperature range. For example, the diffusion coefficients of oxygen in a hyper-stoichiometric composition $UO_{2.1}$ are 1.24×10^{-3} and 4.03×10^{-3} at 1600K and 2000K respectively, which is roughly a difference of a multiple of 3. In order to emphasize this behavior, the diffusion of oxygen was plotted as a function of composition in Fig. 6 (b). This finding agrees with our hypothesis, which states that defects in the composition actually mitigate diffusion at a lower temperature, which means a lower cost of activation energy. As we can see, the oxygen is easily diffusible through the vacancies formed in the hypo-stoichiometric structures. By comparison, the effect of the composition with interstitial oxygen ions is slightly weaker; however it still maintains a favorable rate, as opposed to the stoichiometric structure.

In order to confirm the validity of these results, the natural log of the diffusion coefficients at each composition was plotted against the inverse of temperature.

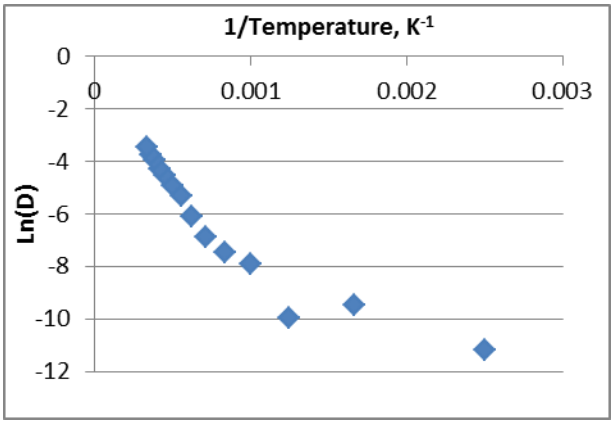

Fig. 7 (a). Sample plot of the natural log of the diffusion coefficient of hypo-stoichiometric UO1.97 as a function of the inverse of temperature

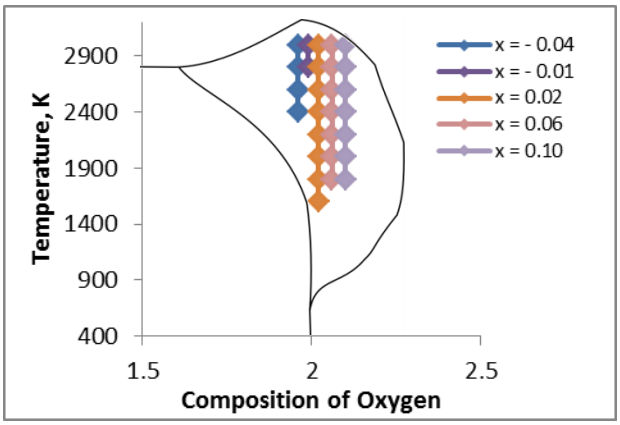

Fig. 7 (b). The temperature ranges at which the displayed compositions of non-stoichiometric UO2±x demonstrate Arrhenius behavior within the constraints of the areas of stability of the FCC structure according to the phase diagram [12]

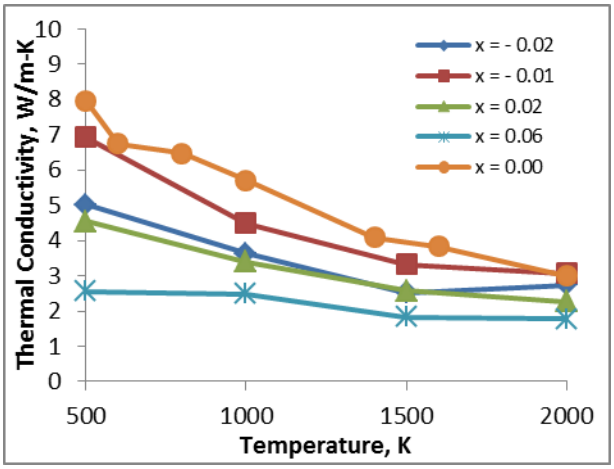

Fig. 8 (a). Thermal conductivity of different non-stoichiometric compositions of UO2±x as a function of temperature

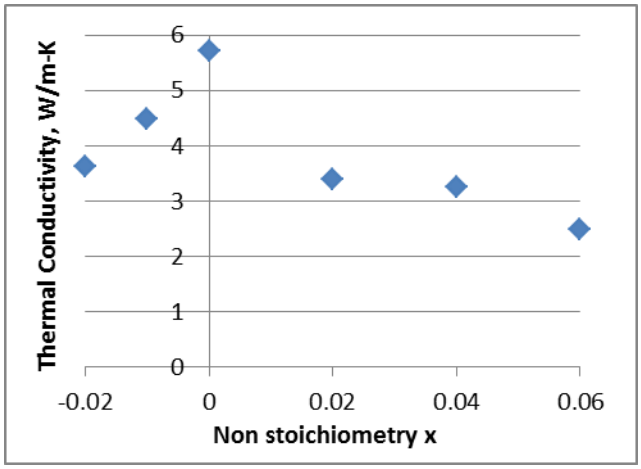

Fig. 8 (b). Thermal conductivity at 1000K as a function of composition

Hypothetically, such plots are assumed to determine the Arrhenius behavior of the temperature-diffusion correlation. Fig. 7 (a) demonstrates a sample plot of ln(*D*) as a function of 1/T of hypo-stoichiometric $UO_{1.97}$. It is obvious from this plot that Arrhenius behavior is only observed within high temperatures. The temperature ranges at which the plots of different compositions demonstrated a linear decay were then compared with the phase diagram of $UO_{2\pm x}$. [12] The U-O phase diagram depicts the temperatures and compositions at which uranium dioxide maintains its FCC structure. The results obtained from the calculations performed in this work consistently contoured the constraints of the FCC structure phase, as described by the diagram (Fig. 7 (b)).

3.4. Thermal conductivity of uranium dioxide

In the present work, the Green-Kubo [13] approach was applied for the investigation of the effects of change in composition on thermal conductivity of uranium dioxide. This method was adopted from Nichenko's [2] evaluation of thermal conductivity through an equilibrium molecular dynamics simulation. This approach assumes that the thermal conductivity can be calculated as a

time function of the auto- correlation of the energy current, as shown in the following equation:

$$\kappa = \frac{1}{3k_B T^2 V}\int_0^\infty dt\left\langle \vec{J}(t)\cdot\vec{J}(0)\right\rangle \quad (5)$$

The values of the energy current, $J(t)$ and $J(0)$, were extracted directly from a calculation performed in LAMMPS. Then, in order to calculate the integral, the trapezoidal rule approximation was used. The calculated values were investigated as functions of temperature and composition. Fig. 8 (a) shows the calculated thermal conductivity plotted against temperature, at several different compositions. This plot clearly demonstrates that the increase in the temperature along with the change in composition have a negative effect on thermal conductivity of uranium dioxide at different compositions. The values obtained from the present calculation closely follow those described in Nichenko's work. In order to emphasize this effect, thermal conductivity of uranium dioxide at 1000K was plotted as a function of composition. To reiterate the previous results, Fig. 8 (b) demonstrates the behavior of thermal conductivity, which agrees with our hypothesis and the previous studies of the effect of composition change on thermal conductivity.

4. Conclusions

For uranium dioxide at its stable fluorite structure, molecular dynamics simulations were performed in order to evaluate the thermal expansion, heat capacity, diffusivity, and thermal conductivity in terms of temperature and the non-stoichiometry of oxygen. The calculations of thermal expansion in terms of the lattice constants show that the lattice constants generally increase with the increase in temperature for any composition, but when different compositions are evaluated at the same temperature, a decrease in the lattice constant caused by the increase in the non-stoichiometric oxygen parameter (x) is observed. The observation of the effect of temperature increase on the heat capacity of uranium dioxide demonstrated an increasing pattern with the increase in temperature, regardless of composition. However, when the behavior of different compositions was examined at a fixed temperature, a negative effect on the heat capacity was observed which can be attributed to the change in composition (for both hypo- and hyper-stoichiometric cases). In contrast with the conclusions regarding the analysis of the previous two properties, a rather favorable effect of the change in composition on the diffusion of oxygen was observed. Namely, the self-diffusion of oxygen occurs at a much lower temperature in the defective structures (both hypo- and hyper-stoichiometric) than it does in the perfect one. The calculations demonstrated that oxygen diffusivity exhibits an Arrhenius behavior in the stability region of the fluorite phase. The calculations also show the effect of temperature increase and the variation in composition on thermal conductivity of the fuel, where both demonstrated a negative effect on the thermal conductivity of the fuel.

Acknowledgments

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References

[1] T. Arima, S. Yamasaki, Y. Inagaki and K. Idemitsu, "Evaluation of thermal properties of UO2 and PuO2 by equilibrium molecular dynamics simulations from 300 to 2000K," *Journal of Alloys and Compounds,* vol. 400, no. 1-2, pp. 43-50, September 2005.

[2] S. Nichenko and S. Dragos, "Molecular Dynamics study of the effects of non-stoichiometry and oxygen Frenkel pairs on the thermal conductivity of uranium dioxide," *Journal of Nuclear Materials,* vol. 433, no. 1-3, pp. 297-304, February 2013.

[3] S. Plimpton, A. Thompson and P. Crozier, "Large-scale Atomic/Molecular Massively parallel Simulator," Sandia National Laboratory, 2013.

[4] B. Willis, *Acta Cryst.,* vol. 34, pp. 88-90, 1997.

[5] H. Inaba, R. Sagawa, H. Hayashi and K. Kawamura, "Molecular dynamics simulation of gadolinia-doped ceria," *Solid State Ionics,* vol. 122, no. 1-4, pp. 95-103, July 1999.

[6] T. Yamashita, N. Nitani, T. Tsuji and H. Inagaki, "Thermal expansions of NpO2 and some other actinide dioxides," *Journal of Nuclear Materials,* vol. 245, no. 1, pp. 72-78, May 1997.

[7] E. Yakub, C. Ronchi and D. Staicu, "Computer simulation of defects formation and equilibrium in non-stoichiometric uranium dioxide," *Journal of Nuclear Materials,* vol. 389, no. 1, pp. 119-126, 15 May 2009.

[8] D. Martin, "The thermal expansion of solid UO2 and (U, Pu) mixed oxides — a review and recommendations," *Journal of Nuclear Materials,* vol. 152, no. 2-3, pp. 94-101, May 1988.

[9] J. Fink, "Thermophysical properties of uranium dioxide," *Journal of Nuclear Materials,* vol. 279, no. 1, pp. 1-18, March 2000.

[10] C. Basak, A. Sengupta and H. Kamath, "Classical molecular dynamics simulation of UO2 to predict thermophysical properties," *Journal of Alloys and Compounds,* vol. 360, no. 1-2, pp. 210-216, 6 October 2003.

[11] M. Bredig, in *Colloq. Int. C. N. R. S.*, 1971.

[12] E. Moore, C. Geuneau and J. Crocombette, "Diffusion model of the non-stoichiometric uranium dioxide," *Journal of Solid State Chemistry,* vol. 203, pp. 145-153, July 2013.

[13] M. Green, "Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids," *Journal of Chemical Physics,* vol. 22, no. 3, p. 398, March 1954.